Raman Microscopy Study of Plastics in Museum Collections

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The work presented here evaluates the spectral performance of two handheld Raman spectrometers for the *in-situ* identification of plastic objects in Museum Collections. The instruments evaluated were the *ReporteR* (Intevac) and *FirstDefender* (Ahura), originally manufactured for the pharmaceutical and hazmat fields. A set of 100 different reference plastics, including the plastic families most commonly found in Museums (cellulose-based, polystyrene, polypropylene, polycarbonate, silicone, etc) were tested with the two handheld instruments, and a bench-top instrument (Renishaw *In-Via*) for comparison.

FirstDefender by Ahura *ReporteR* by Intevac

Technical comparative of the two portable Raman devices

	FirstDefender -Ahura-	Reporter -Intevac-
Spectral range	250-2875 cm^{-1}	200-2000 cm^{-1}
Spectra resolution	7-10.5 cm^{-1} accross range	~12-15 cm^{-1} across range
Laser excitation wavelenght	785 nm +/- 0.5 nm, 2 cm^{-1} linewidth, stability<0.1 cm^{-1}	785 nm, stability <0.2 cm^{-1}
Laser output power	300 mW or lower	~60 mW or lower
Collection optics	NA=0.33; 18 mm working distance, 0.2-2.5 mm spot size, fiber optic probe head	NA=0.4; right angle and point and shoot pressed against samples, <0.05 mm spot size
Battery	Internal, rechargeable 7.4 V Li Ion battery> 5 hours (25°C)	Internal rechargeable Li Ion battery> ~ 4 hours (25°C)
Weight	<1.8 kg	0.312 gr
Size	30x15x7.6 cm	15.2x7.6x4.4 cm
GratingDetector	Detector - Silicon CCD linear array, Grating - holographic, 1200 lines/mm	Detector - Silicon CCD linear array, Grating - holographic, 1800 lines/mm
Operating temperature	" -20" to +40 °C	
Exposure	Manual/automatique, minimun 100 ms	
Camera	No	

The respective performance of each instrument was evaluated against a set of three criteria:

<u>Ergonomics and collection optics</u>: The small size and light weight of the *ReporteR* are a major asset in comparison with the *FirstDefender*. However, the *FirstDefender* provides a set of optic accessories such as the fiber optic probe, that significantly help access certain areas of intricate artworks (although 50% of the laser power is lost when using the fiber optic probe).

<u>Spectral range</u>: The wider spectral range (200-2800 cm^{-1}) provided by the *FirstDefender* represents an advantage in the study of plastics, because a few groups such as C≡C, C≡N, N-H or S-H have bands above 2000 cm^{-1} (an area not covered by the *ReporteR*).

<u>Spectral resolution</u>: Although less intense (the signal/noise ratio is higher in the *ReporteR*) the spectrum recorded with the *FirstDefender* often shows a better spectral resolution than the *ReporteR*: the FWHM (Full Width at Half Maximum) for the most intense band of cellulose acetate (at 1040 cm^{-1}) are 10, 20 and 12 cm^{-1} for the bench-top Raman, the *ReporteR* and the *FirstDefender* respectively (Fig 1).

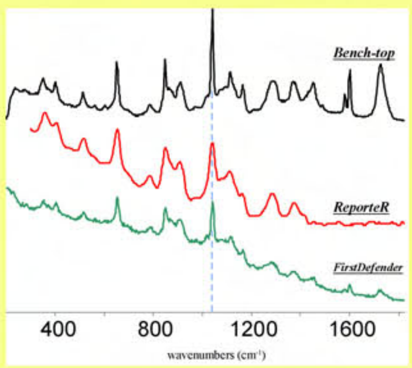

Fig 1. Raman spectra of a Cellulose Acetate plastic analyzed with the two portable devices and the bench-top Raman.

In addition to the in-lab analyses, *in-situ* measurements on real objects were performed at the Los Angeles County Museum of Art (LACMA, Los Angeles) and the Musée d'Art Moderne et d'Art Contemporain (MAMAC, Nice). These studies are part of a large collaborative project, POPART (Preservation Of Plastic ARTefacts in museum collections), recently established in order to investigate the conservation issues of plastic objects (http://popart.mnhn.fr). The *in-situ* analyses showed a few additional drawbacks in comparison to the in-lab analyses on reference plastics. The difficulties were mainly due to dust remaining in the anfractuosities of the piece of art, the high heterogeneity in the composition of some objects, or the fragile state of some plastic objects that prevented any contact with the instrument.

Photo: R. Rivenc

Some objects provided good Raman spectra, e.g. *Venus aux ongles rouges* by Niki de Saint Phalle was characterized by using the *FirstDefender* as being composed of polyester.

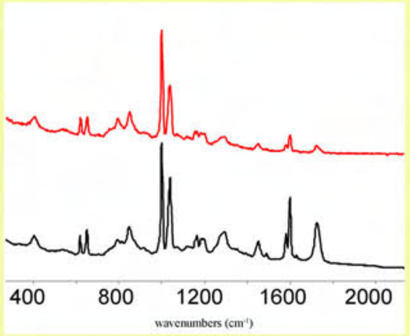

Fig 2. Raman spectrum acquired with the *FirstDefender* on "*Venus aux ongles rouges*" (top) in comparaison with a reference spectrum of polyester (bottom).

The comparison of these two instruments also helped in understanding that the surface treatment, the type of pigmentation, the production method or the final shape of the object can fundamentally affect the quality of the Raman spectrum. That was noticed for example when analyzing four urethane elastomere thermosplatics manufactured under different shapes and coloration (hard dense, soft leather like and fibrous forms) (Fig 3).

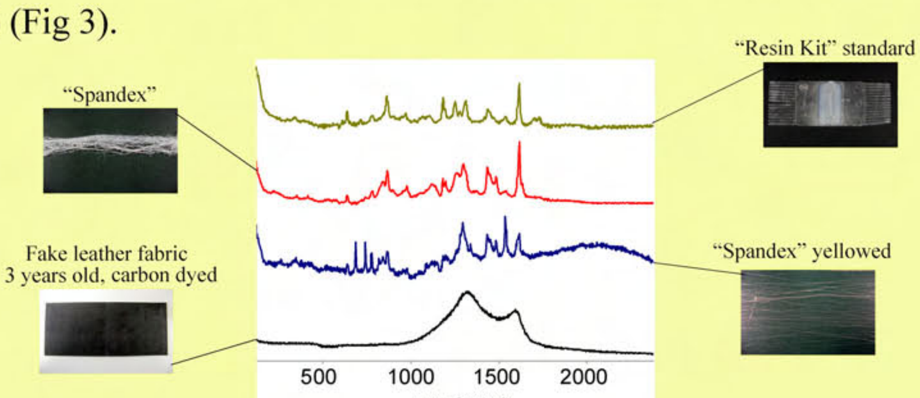

Fig 3. Raman spectra of four different shaped and colored urethane thermoplastics

It would be unrealistic to expect any portable Raman instrument to produce spectra of a similar quality to those acquired with a bench-top instrument. Nevertheless, instrument size and hardware improvement (e.g. detector sensitivity) are both constantly improving. A close collaboration between conservation scientists and instrument manufacturers would clearly improve these portable instruments further for this specialized field of application.